

Multi-Atom Resonant Photoemission: Theory and Systematics

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The recently discovered inter-atomic multi-atom resonant photoemission (MARPE) effect [1] has been the subject of theoretical investigation that has permitted to establish the relevant elements involved in this phenomenon [2], where core photoelectron intensities are enhanced when the photon energy is tuned to a core-level absorption edge of non-identical neighboring atoms, thus enabling a direct determination of near-neighbor atomic identities. Both the multi-atom character of MARPE and relativistic retardation effects in the photon and electron interactions in the resonant channel have been shown to be crucial. In particular, they lead to constructive interference of resonant and direct emission in the MnO example under study, resulting in experimentally-observed peak-intensity enhancements of the order of 40-65% and spectral shapes similar to the corresponding x-ray absorption profiles.

In a first discussion of the theory of MARPE [1] the conventional model used to describe the well-known intra-atomic single-atom resonant photoemission (SARPE) [3-6] has been generalized to apply to this new phenomenon. Specifically, photoemission is assumed to occur via absorption of a single photon and two different channels that leave the crystal in exactly the same final quantum state, and thus have to be added coherently: the direct emission channel in which an O1s electron absorbs a photon and the resonant emission channel that is assisted by the Mn2p→Mn3d resonance. In the resonant channel, the photon promotes a Mn2p electron to a Mn3d state, from which it decays instantaneously to refill the Mn2p hole, while exciting the O1s electron to the continuum. This decay can also be termed an inter-atomic auto-ionization process (AI), and it is thus closely related to the much weaker inter-atomic Auger processes. Notice that several Mn neighbors of the emitter must be summed coherently. A first estimate from such a theoretical treatment gives an energy-integrated effect of 2.5%, or about 4 times less than experiment [1]. However, the model used previously did not permit treating the precise many-electron states and energies involved, and so could not predict the form of the spectral enhancements as a function of energy. We have shown that this model was too simplified as to the electromagnetic interactions involved. The present work thus introduces a significantly more quantitative first-principles approach to the theory of MARPE that yields very good agreement with experiment in most respects and permits further assessing the systematics of this new phenomenon. In particular, many-electron configuration interaction states are used to describe the Mn2p→Mn3d excitation and relativistic effects in photon excitation and auto-ionization are included.

Use of the Kramers-Heisenberg formula has been made to calculate photoelectron intensities, where the intermediate states are obtained within a configuration interaction scheme for an octahedral cluster formed by a Mn²⁺ ion surrounded by six O²⁻ ions. Both the interaction with the external photon and the inter-atomic interaction incorporate

retardation effects, which are important due to the combination of relatively large inter-atomic distances and photon energies; actually, the change in the phase of a photon that travels across the nearest-neighbor distance in MnO is 42° when the photon energy matches the Mn2p resonance. The interaction between dipole currents induced during the two-electron transition dominates over the charge-charge term. Further details on the theory are given elsewhere [2].

The absorption and re-emission of a photon by Mn in MnO is described in terms of the Mn polarizability, which enters the Kramers-Heisenberg formula. The imaginary part of this quantity is roughly proportional to the absorption coefficient, as can be seen in Fig. 1(a), where experimental data are compared with this theory.

The results of our calculations of the MARPE effect for two different measurement geometries are shown in Figs. 1(b)-(c). Plotted is the quantity I/I_0 , where I is the actual O1s intensity and I_0 is the non-resonant background under it. Curves are shown for both a full sum over all Mn atoms, and a sum limited to a distance of $10d$ from the emitter, where d is the nearest-neighbor distance. The predicted enhancements follow quite closely the shape of the x-ray absorption profile, showing little evidence of the constructive/destructive interference patterns that are often seen in so-called Fano profiles [3], in agreement with experiment [1]. In general, the more limited sum agrees better with experiment as to both peak positions and intensities, suggesting an effectively more rapid convergence with distance in experiment. In magnitude, there is also excellent agreement for the geometry in Fig. 2(b) for an x-ray incidence angle of 20° , but in Fig. 2(c) the principal Mn2p_{3/2} peak is predicted to be too weak by a factor of 2 for an incidence angle of 40° . The possible reasons for this discrepancy are inaccuracies in our treatment of nearest-neighbor effects and the O1s hole state, multiple scattering and resultant phase averaging of the radiation (much enhanced at the resonance), and neglect of atomic vibrational motion.

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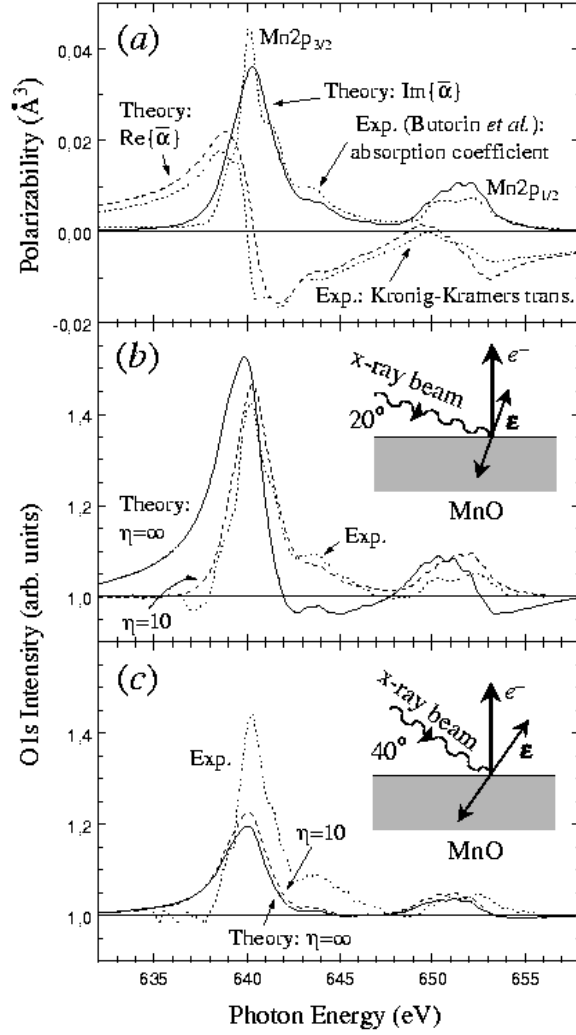


Figure 1. (a) Real (dashed curve) and imaginary (solid curve) parts of the average polarizability of Mn^{2+} in MnO, calculated using a configuration interaction scheme [6], as compared with the experimental absorption coefficient [7] and its Kronig-Kramers transformation (dotted curves). (b) Enhancement in the O1s photoelectron intensity emitted along the normal of a MnO(001) surface illuminated with linearly polarized light incident at an angle of 20° with respect to the surface. The polarization vector lies in the plane containing [100] and [001]. The experimental result [1] (dotted curve) is compared with theoretical curves for a full sum over all Mn atoms in each plane (solid curve, $\eta = \infty$) and for a sum only out to 10 nearest-neighbor distances (dashed curve, $\eta = 10$). (c) The same as (b) for an incidence angle of 40°.